



Rational design and preparation of nanoheterostructures based on zinc titanate for solar-driven photocatalytic conversion of CO₂ to valuable fuels

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ABSTRACT

Photocatalytic reduction of CO₂ with H₂O on photocatalysts to produce fuels presents great potential to simultaneously address energy and environmental issues. Herein, zinc titanate-based heterostructured nanohybrids including Zn₂Ti₃O₈/ZnTiO₃ and Zn₂TiO₄/R-TiO₂ were designed and prepared through a two-step chemical route. When used as photocatalyst for converting CO₂ with H₂O under UV-light irradiation, the zinc titanate-based heterostructured nanohybrids show high photocatalytic performance, with CH₄ and CO yields significantly higher than those obtained with Zn₂Ti₃O₈, Zn₂TiO₄, and rutile TiO₂ as the photocatalysts. The existence of heterojunctions in the nanohybrids was demonstrated by experimental results, and electrochemical impedance spectra also reveal a favorable zinc titanate-based heterostructure. Moreover, based on theoretical calculations, the observed reduced band gap further revealed the effective light-absorption of the heterostructured nanohybrids in CO₂ reduction. It is thus concluded that the synergistic effect of the heterostructure promotes charge separation and fast electron transport, resulting in its enhanced photocatalytic performance in CO₂ reduction.

1. Introduction

Finding a low cost, renewable and clean energy source as an alternative to fossil fuels remains a huge challenge for researchers [1,2]. Conversion of CO₂ into fuels (eg. CH₄, CO, CH₃OH) undoubtedly presents a great potential to solve the growing energy crisis [3]. Currently, various conversion strategies have been developed to chemically reduce CO₂ [4]. Among them, photocatalytic CO₂ reduction via artificial photosynthesis is considered one of the most promising techniques for renewable fuels production. Many photocatalysts have been studied for CO₂ photoreduction [2,5–8], but TiO₂ remains the most convenient candidate considering the stability, cost, and nontoxicity [9]. However, the conversion efficiency of CO₂ to value added carbon products under the catalysis of TiO₂ is still very low due to fast electron–hole recombination.

To improve the efficiency of solar fuels production, many design strategies, including band-structure engineering, heterostructured constructing and nano-structuralization, have been proposed to develop photocatalyst materials, in which the one the most widely used is to construct photocatalyst heterojunctions [10,11]. Studies [12–14] have demonstrated that the resulting heterojunctions in those composites can remarkably suppress the recombination of electron-hole pairs and boost

the diffusion of photogenerated carriers. In recent years, titanates have been widely investigated as a potential alternative to TiO₂ for photocatalytic reaction due to their adjustable composition and electronic structure properties [9]. Especially, due to its excellent optical, electrical and physical chemistry properties, zinc-based titanate has been paid increasing attention [15,16]. Generally, zinc titanate exists in three different phases including ZnTiO₃ (hexagonal), Zn₂Ti₃O₈ (cubic), and Zn₂TiO₄ (face-centered cubic). ZnTiO₃ is one of the promising materials and has been widely used for gas sensor, nonlinear optics and catalytic sorbents [17–19]. Zn₂Ti₃O₈ is a metastable form, and has received increasing attention since it exhibits suitable band-gap for photocatalytic water splitting [15]. Compared with the reported ZnTiO₃ and Zn₂Ti₃O₈, cubic spinel Zn₂TiO₄ seems to be most stable phase. When Zn₂Ti₃O₈ is heated at high temperature, it will decompose into Zn₂TiO₄, rutile-type TiO₂ and other phases [20]. Among the three different crystalline phases of zinc titanate, Zn₂Ti₃O₈ has a relatively high reducing potential [21] and is thermodynamically able to photoreduce CO₂ without additional reductants, and the potential of the valence band holes is much more positive than the water oxidation potential. Recent research also shows that the valence band of Zn₂Ti₃O₈ is more positive and the conduction band is more negative than the respective bands of anatase TiO₂ [22]. This can be conducive to the reduction of

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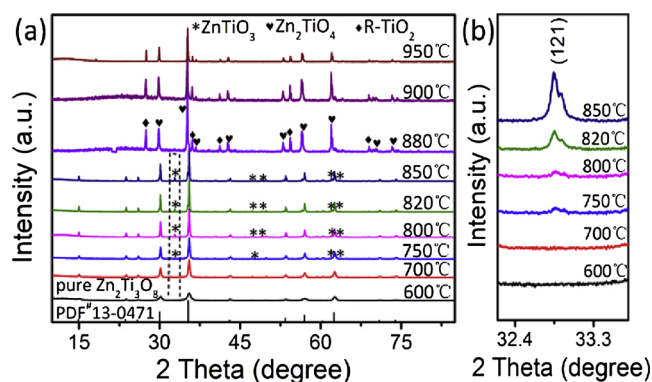


Fig. 1. (a) XRD patterns of products obtained at different calcination temperatures between 600°C and 950°C. (b) The enlarged part for XRD patterns of corresponding products ranging from $2\theta = 32.1^\circ$ to 33.8° .

CO₂ driven by solar energy. Therefore, design of zinc-based titanate and their composites can be a very feasible and effective approach to achieve high-performance photocatalysts.

Herein, we developed an effective strategy to prepare zinc titanate-based composites. The strategy is a two-step chemical procedure, including hydrothermal reaction of butyl titanate with zinc acetate and high-temperature calcination under air flow. The resulting photocatalyst showed high performance in the photoconversion of CO₂ and water to CO and CH₄. Analysis reveals that the high performance is attributed to the excellent charge separation and fast electron transport in the photocatalysts due to the formation of heterojunctions. Additionally, DFT calculations reveal that the zinc titanate-based heterostructured nanohybrids have a suitable band-gap. Reduced band gaps were observed in the zinc titanate-based heterostructured nanohybrids, implying that the heterostructured nanohybrid can increase the wavelength of absorbed light, thereby achieving high photo-conversion efficiency.

2. Experimental section

2.1. Catalyst preparation

Sodium titanate nanobelt (Fig. S1) was prepared by a simple modified hydrothermal route based on previous report [23]. Typical procedures of preparing the sodium titanate nanobelt are as follows: 1.5 g of NaOH was added into CH₃CH₂CH₂OH/H₂O solution (55 mL isopropyl alcohol and 10 mL deionized water) under stirring. Subsequently, 2.1 g of butyl titanate was added to the above solution and the mixture was stirred for 30 min. Then, the mixture was transferred into a 100-mL Teflon-lined stainless-steel autoclave. The autoclave was sealed and maintained at 180°C for 24 h, and then cooled to room temperature. The final products were filtered, washed with deionized water and dried at 70 °C for 12 h.

Synthesis of zinc titanate-based heterostructures: In a typical two-step process, the as-obtained sodium titanate (0.151 g) and zinc acetate (3.5 mmol) were added to 18 mL of deionized water, and the mixture was stirred for 1 h. The solution was then transferred into a 25-mL Teflon-lined stainless steel autoclave and maintained at 200°C for 24 h in an oven. After natural cooling, the product was washed repeatedly with distilled water and then dried at 70°C for 12 h. In the next step, the dried product was calcined at 600, 700, 750, 800, 820, 840, 880, 900 and 950 °C, respectively, and maintained for 3 h at each temperature. Different samples were thus obtained. For comparison, the rutile TiO₂ (R-TiO₂) was prepared by heating commercial anatase TiO₂ at 950°C for 6 h. The bulk Zn₂TiO₄ was synthesized by heating a stoichiometric mixture of TiO₂ and ZnO at 1200 °C for 24 h.

2.2. Characterization

X-ray powder diffraction (XRD) was taken on a Bruker D8 Focus power diffractometer with Cu K α radiation (40 kV/mA) to verify the crystal structure of obtained samples. To investigate the surface chemical composition of samples, X-ray photoelectron spectroscopy (XPS)

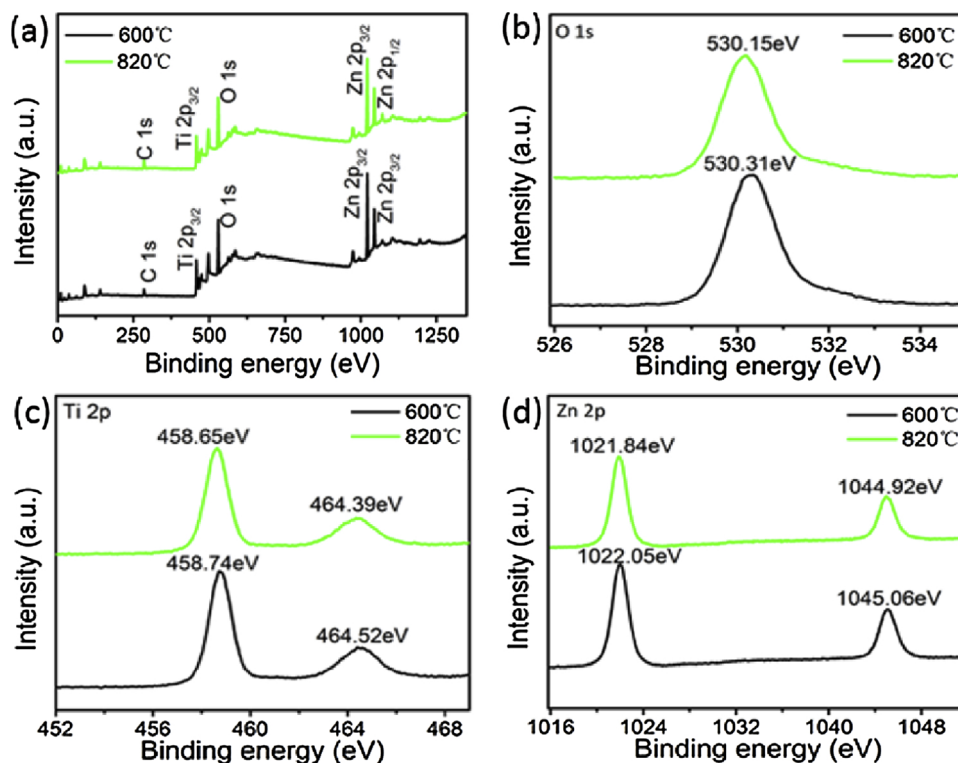


Fig. 2. (a) Wide scan XPS survey spectra of Zn₂Ti₃O₈ and Zn₂Ti₃O₈/ZnTiO₃ (calcined at 600°C and 820°C, respectively). High resolution XPS spectra of products: (b) O 1s, (c) Ti 2p, and (d) Zn 2p of Zn₂Ti₃O₈ obtained at 600°C and Zn₂Ti₃O₈/ZnTiO₃ obtained at 820 °C.

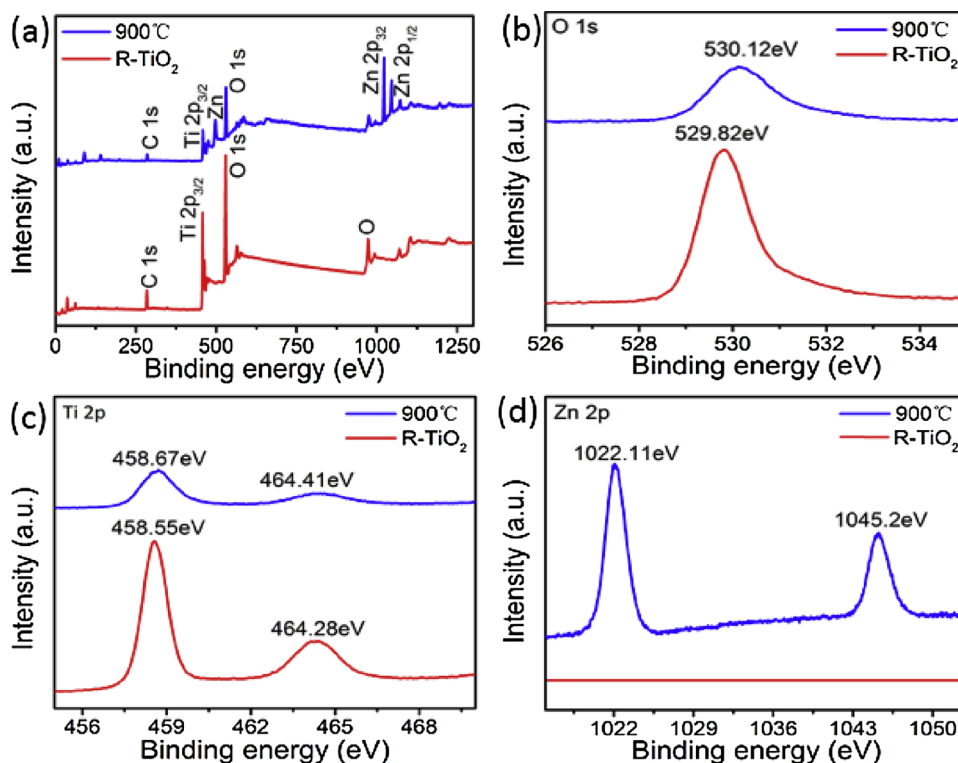


Fig. 3. (a) Wide scan XPS survey spectra of $\text{Zn}_2\text{TiO}_4/\text{R-TiO}_2$ obtained at calcination temperature of 900°C and R-TiO_2 . XPS spectra of $\text{Zn}_2\text{TiO}_4/\text{R-TiO}_2$ obtained at 900°C and R-TiO_2 : (b) O 1s, (c) Ti 2p, and (d) Zn 2p.

was performed on an ESCALAB 250 Xi (Thermo Fisher Scientific) electron spectrometer with Al K α ($h\nu = 1486.6\text{ eV}$). The diffuse reflectance spectra of samples during a range from 200 to 800 nm were recorded using a Varian Cary 500 Scan UV/Vis system. In addition, size and morphologies of samples were characterized by the transmission electron microscope (TEM, FEI Technai G2 F20), scanning electron microscope (SEM, JSM-5600LV), and high-resolution transmission electron microscope (HRTEM, FEI Technai G2 F20) operated at 200 kV along with selected area electron diffraction (SAED). Raman studies were carried out on a Horiba Jobin Yvon LabRAM HR800 spectrometer (France) with a 532-nm laser as the excitation source. The N_2 adsorption-desorption isotherms were measured at liquid nitrogen temperature (-197°C) by using Micromeritics apparatus model ASAP 2020 equipment and the Brunauer–Emmett–Teller (BET) method. The CO_2 adsorption isotherms were measured at 0°C .

2.3. Computational method

The density functional theory (DFT) calculation was performed by CP2K/Quickstep package [24]. Hubbard U correction was applied to d orbitals of Ti and Zn atoms with the corresponding U values set to 3.5 eV and 7.0 eV, respectively [24,25]. A 320 Ry cut off energy was used for auxiliary basis set of plane waves. The PBE exchange correlation functional was used in all calculations. The wave functions of valence electrons were expanded in terms of Gaussian function with molecularly optimized double-zeta polarized basis sets (m-DZVP) [26]. In addition, core electrons were described with the norm-conserving Goedecker, Teter, and Hutter (GTH) pseudopotentials [27].

2.4. Photocatalytic activity testing

By using as-obtained samples for photocatalytic CO_2 reduction at ambient temperature under UV-light radiation (Philips Co., TUV 4 W/G4T5), their photocatalytic activities were evaluated. In a typical photocatalytic experiment, the quartz glass reactor was first heated at

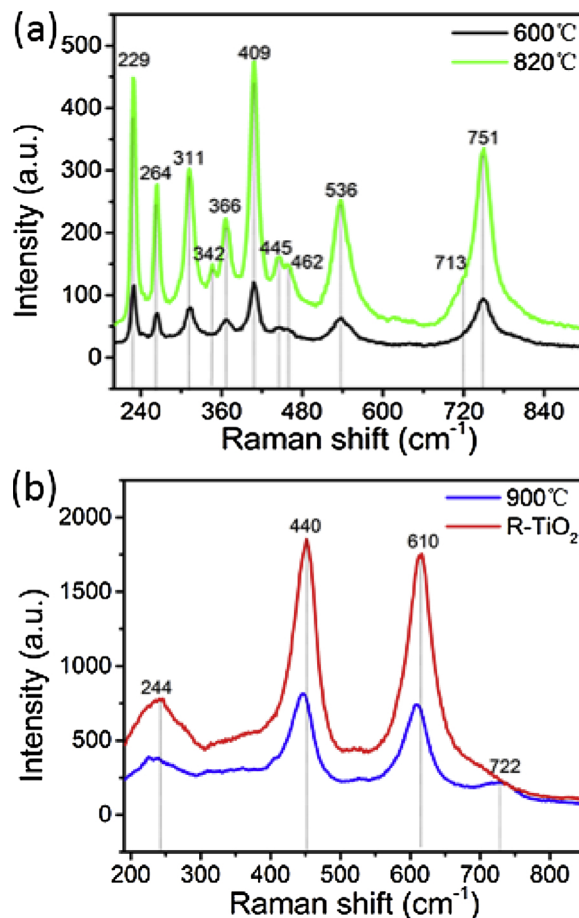


Fig. 4. Raman spectra of the synthesized samples: (a) $\text{Zn}_2\text{Ti}_3\text{O}_8$ obtained at 600°C and $\text{Zn}_2\text{Ti}_3\text{O}_8/\text{ZnTiO}_3$ obtained at 820°C . (b) $\text{Zn}_2\text{TiO}_4/\text{R-TiO}_2$ obtained at 900°C and R-TiO_2 .

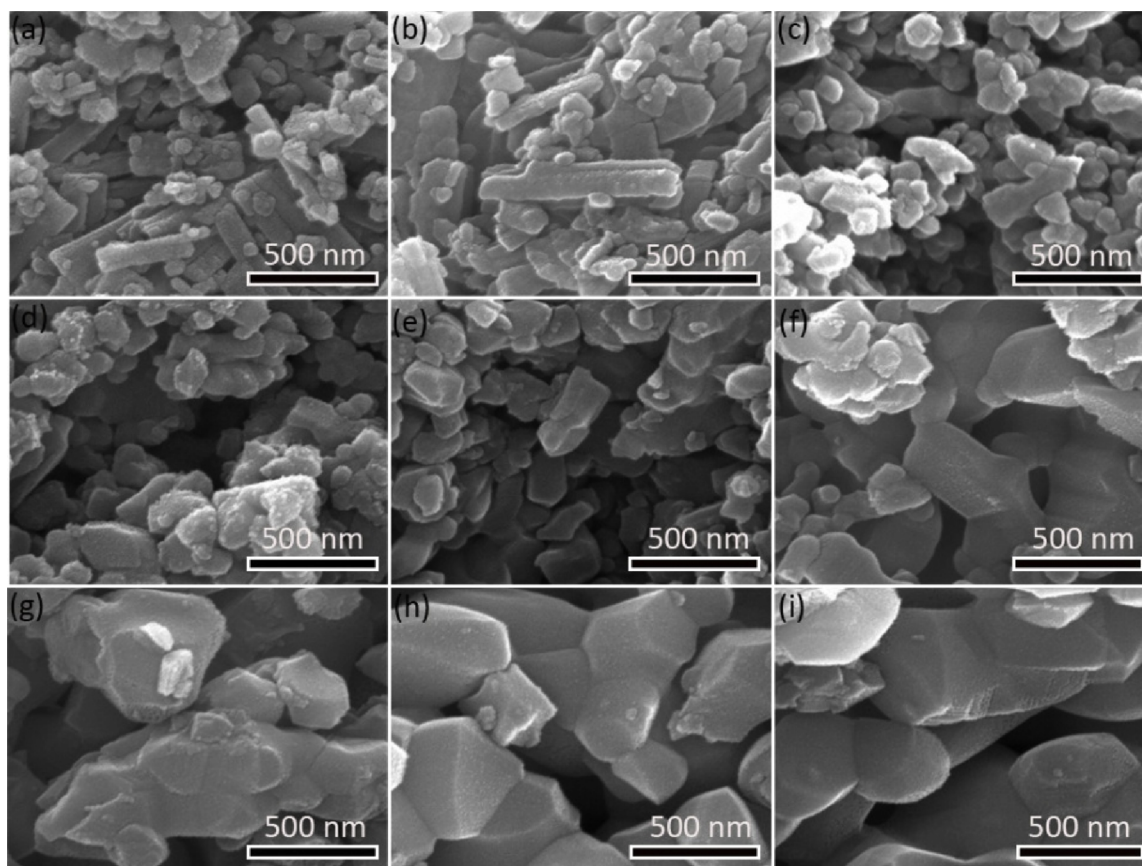


Fig. 5. Typical SEM images of the as-obtained products at different annealing temperatures (a) 600 °C (b) 700 °C (c) 750 °C (d) 800 °C (e) 820 °C (f) 850 °C (g) 880 °C (h) 900 °C and (i) 950 °C.

500 °C for 3 h in air to remove any possible traces of organic matter from the inner walls of reactor. Then, 50 mg of the as-prepared photocatalyst powder was dispersed in a 25-mL pyrex glass reactor with a silicone rubber septum. Subsequently, the whole system was subjected to vacuum degassing and then backfilling with pure CO₂ gas (99.995%) to remove the air inside. The evacuation-filling process was repeated four times, and then the reactor was backfilled with high-purity CO₂ (1 bar) after the last cycle. Finally, 20 μ L of liquid deionized water was injected into the reactor with a microsyringe, and deionized water was gasified by heating with a hair dryer. Prior to illumination irradiation, magnetic stirring was performed in dark for 30 min for establishment of adsorption/desorption equilibrium. Then, photocatalytic reaction was carried out for 4 h under UV-light irradiation ($\lambda = 254$ nm, $4\text{ W} \times 4 = 16\text{ W}$). After the irradiation, for subsequent gas concentration analysis, 0.5 mL of gas was taken out from the glass reactor by a gas chromatography (GC-7890A, Shimadzu) equipped with a flame ionization detector (FID) and a capillary column (GC-GASPRO, 30 m \times 0.320 mm). The outlet gas was determined to contain CO and CH₄. The product gas was calibrated with a standard gas mixture, its identity was determined with the retention time, and it was then analyzed quantitatively with external standard method. In the test of the stability of photocatalyst, the photocatalytic reaction was evacuated at ambient temperature for 4 h and refilled with high-purity CO₂ and liquid deionized water in each cycle.

2.5. Electrochemical impedance spectra

An electrochemical impedance spectrometer (EIS) is generally used to characterize the interfacial electrochemical properties of electrodes. The EIS tests were carried out by a three-electrode electrochemical system in 5.0 mmol L⁻¹ Fe(CN)₆^{3-/4-} mixture containing 0.1 mol L⁻¹

KCl solution with saturated calomel electrode (SCE) and platinum (Pt) column as the reference electrode and counter electrode, respectively.

3. Results and discussion

Fig. 1 shows the XRD patterns of thermally treated products of zinc titanate precursor obtained at different calcination temperatures between 600 °C and 950 °C. In Fig. 1a, the samples calcined at 600 and 700 °C only possess a cubic crystal structure as Zn₂Ti₃O₈ (PDF#13-0471), and it can be confirmed that both samples are pure cubic Zn₂Ti₃O₈ crystals. As the calcination temperature increased to 750 °C, hexagonal ZnTiO₃ (PDF#25-0671) began to be formed. This means that heterostructured Zn₂Ti₃O₈/ZnTiO₃ nanohybrids can be obtained in situ. The peak intensities of ZnTiO₃ was continuously increased as calcination temperature-increased from 750 to 850 °C (Fig. 1b). As the calcination temperature further increased from 850 to 950 °C, cubic-spinel phase Zn₂TiO₄ (PDF#25-1164) and R-TiO₂ (PDF#21-1276) were formed simultaneously, which were mainly resulted from the decomposition of Zn₂Ti₃O₈ and ZnTiO₃ [28]. In sum, by changing the temperature in the range of 600 – 950 °C, a series of zinc titanate-based heterostructured nanohybrids including Zn₂Ti₃O₈/ZnTiO₃ and Zn₂TiO₄/R-TiO₂ can be prepared through a facile thermal annealing process. However, the XRD patterns suggest that pure ZnTiO₃ and Zn₂TiO₄ were not formed in the temperature range of 600–950 °C. This might be mainly because pure ZnTiO₃ is a special metastable phase and can easily decompose into Zn₂TiO₄, rutile-type TiO₂ and other phases at high temperature [29,30].

Furthermore, the surface chemical bonding and element binding energy (BE) of the samples were characterized by XPS (Fig. 2). For bare Zn₂Ti₃O₈, the Ti 2p_{3/2} and 2p_{1/2} peaks centered at 458.74 eV and 464.52 eV, respectively, could be assigned to Ti⁴⁺ valence state (Fig. 2c) [31,32], the Zn 2p_{3/2} and Zn 2p_{1/2} peaks positioned at

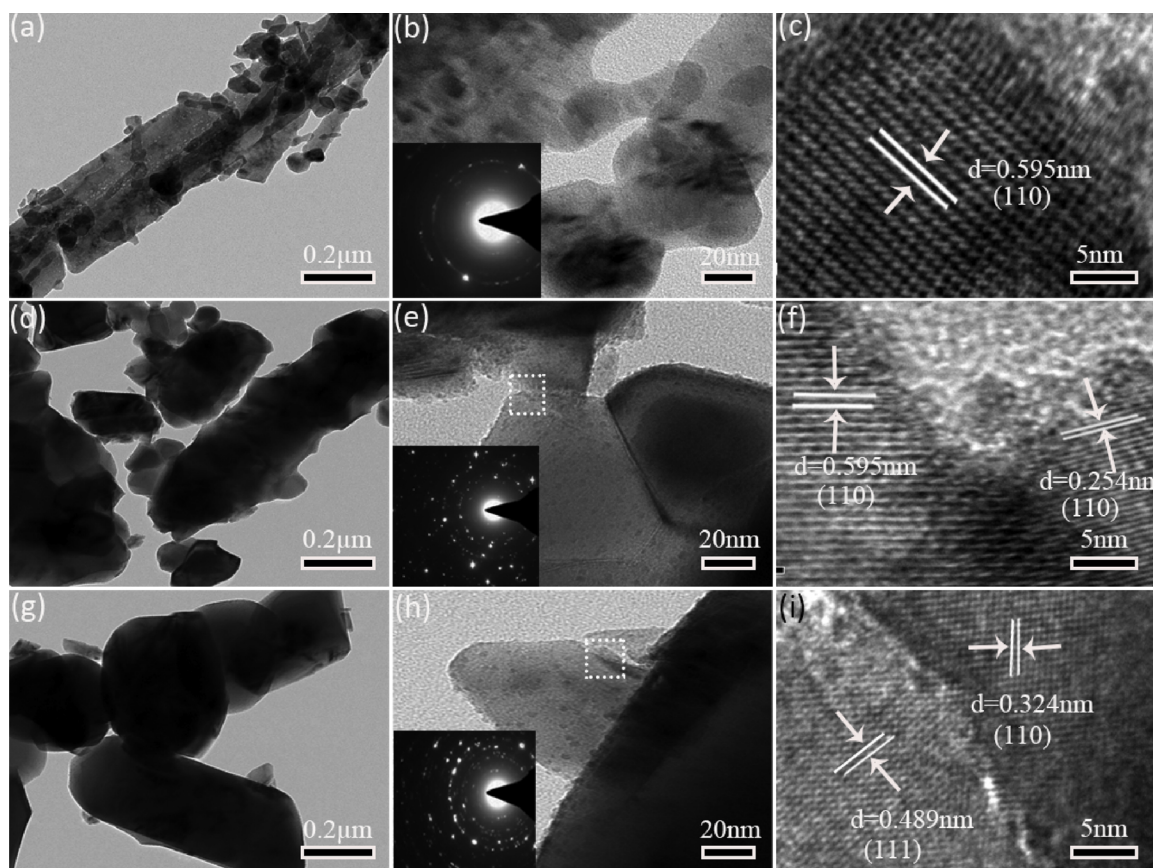


Fig. 6. Typical (a, b) low-magnification TEM and (c) high-resolution TEM images of the $\text{Zn}_2\text{Ti}_3\text{O}_8$ obtained at 600°C. Typical (d, e) low-magnification TEM and (f) high-resolution TEM images of the $\text{Zn}_2\text{Ti}_3\text{O}_8/\text{ZnTiO}_3$ obtained at 820°C. Typical (g, h) low-magnification and (i) high-resolution TEM images of the $\text{Zn}_2\text{TiO}_4/\text{R-TiO}_2$ obtained at 900°C. Insets in panels (b), (e) and (h) are the corresponding SAED patterns.

1022.05 eV and 1045.06 eV (Fig. 2d), respectively, suggest the existence of Zn^{2+} valence state [33]. In comparison, for the $\text{Zn}_2\text{Ti}_3\text{O}_8/\text{ZnTiO}_3$ heterostructure, the peaks of Ti 2p and Zn 2p synchronously shifted slightly toward lower BE, and similar result was also observed in the BE peaks of O 1s (Fig. 2b). The differences in element BE may be mainly attributed to the formation of $\text{Zn}_2\text{Ti}_3\text{O}_8/\text{ZnTiO}_3$ heterostructure, which can lead to the changes of element chemical environments. In the XPS spectra of BiVO_4 [34] and CdS [12] heterostructures, such phenomenon was also observed.

Compared with the XPS peaks of R-TiO₂ (Fig. 3), the XPS peaks of heterostructured $\text{Zn}_2\text{TiO}_4/\text{R-TiO}_2$ sample shifted to higher BE. Specifically, the peak of O 1s shifted from 529.82 eV to 530.12 eV (Fig. 3b), which is probably due to the formation of Zn-O bond (Fig. 3d), usually located at around 530.0 eV [35]. In Fig. 3c, the peak of Ti 2p_{3/2} shifted from 458.55 eV to 458.67 eV and the peak of Ti 2p_{1/2} shifted from 464.28 eV to 464.41 eV. This is probably because the existence of Zn atoms leads to changes in the dispersion of electrons around Ti atoms.

Fig. 4a shows the Raman spectra of bare $\text{Zn}_2\text{Ti}_3\text{O}_8$ and $\text{Zn}_2\text{Ti}_3\text{O}_8/\text{ZnTiO}_3$ composite. Compared with bare $\text{Zn}_2\text{Ti}_3\text{O}_8$, the $\text{Zn}_2\text{Ti}_3\text{O}_8/\text{ZnTiO}_3$ composite presents peaks at around 264, 342, 462 and 713 cm^{-1} in its Raman spectra, which are attributed to the vibration modes of $\nu_4(\text{LO})$, $\nu_2(\text{LO}, \text{TO})$, $\nu_1(\text{TO})$ and $\nu_1(\text{LO})$, respectively and are the characteristic peaks of hexagonal ZnTiO_3 . It is also noted that most of the peaks for $\text{Zn}_2\text{Ti}_3\text{O}_8/\text{ZnTiO}_3$ composite broadened and shifted towards higher frequencies. Fig. 4b shows the Raman spectra of bare R-TiO₂ and $\text{Zn}_2\text{TiO}_4/\text{R-TiO}_2$ composite obtained at 900°C. Peaks at 244, 440 and 610 cm^{-1} are attributed to those of R-TiO₂ [36,37]. For the $\text{Zn}_2\text{TiO}_4/\text{R-TiO}_2$ sample, the peak at 722 cm^{-1} can be ascribed to the spinel-structure Zn_2TiO_4 , corresponding to the normal mode of representation A_{1g} of the space group O_h^F [38]. These results are well

consistent with the XRD analysis as discussed above.

The SEM images of samples obtained at various calcination temperatures are shown in Fig. 5. Fig. 5a displays the typical rod-shaped 1-D nanostructures of $\text{Zn}_2\text{Ti}_3\text{O}_8$ obtained at 600°C, and their lengths typically range from 100 to 300 nm. The $\text{Zn}_2\text{Ti}_3\text{O}_8$ sample obtained at 700°C was found to consist of nanorods coated with nanoparticles (Fig. 5b). As calcination temperature increased from 750 to 850°C, the rod-shaped structures gradually disappeared and many irregular particles and shredded nanorods of $\text{Zn}_2\text{Ti}_3\text{O}_8/\text{ZnTiO}_3$ were formed (Fig. 5c–f). Notably, the particle sizes increase with increasing calcination temperature. As the calcination temperature further increased from 850 to 950°C, the as-obtained $\text{Zn}_2\text{TiO}_4/\text{R-TiO}_2$ samples were found to consist of irregular particles with size of ca. 500 nm (Fig. 5g–i).

TEM images further reveal more details about the nanostructures of $\text{Zn}_2\text{Ti}_3\text{O}_8$, $\text{Zn}_2\text{Ti}_3\text{O}_8/\text{ZnTiO}_3$ and $\text{Zn}_2\text{TiO}_4/\text{R-TiO}_2$ samples. Fig. 6a and b show the typical TEM images of $\text{Zn}_2\text{Ti}_3\text{O}_8$ nanorods obtained at 600°C. The morphological characteristics of the sample are consistent with those revealed by SEM observation. The HRTEM image of the sample is presented in Fig. 6c. The distance between the adjacent lattice fringes is 0.595 nm, which can be assigned to the interplanar distance of the cubic $\text{Zn}_2\text{Ti}_3\text{O}_8$ (110) plane. Fig. 6d and e show TEM images of $\text{Zn}_2\text{Ti}_3\text{O}_8/\text{ZnTiO}_3$ composite obtained at 820°C. It was found that the sample is composed of nanorods and particles. To verify the $\text{Zn}_2\text{Ti}_3\text{O}_8/\text{ZnTiO}_3$ heterostructure revealed by XRD results, HRTEM characterization was performed. As shown in Fig. 6f, explicit heterointerface between the $\text{Zn}_2\text{Ti}_3\text{O}_8$ and ZnTiO_3 phases can be observed, and the interplanar spacing of 0.595 nm and 0.254 nm correspond to (110) plane of $\text{Zn}_2\text{Ti}_3\text{O}_8$ and (110) plane of ZnTiO_3 , respectively. These results indicate the formation of $\text{Zn}_2\text{Ti}_3\text{O}_8/\text{ZnTiO}_3$ heterostructure. For $\text{Zn}_2\text{TiO}_4/\text{R-TiO}_2$ sample obtained at 900°C, the low magnification TEM images

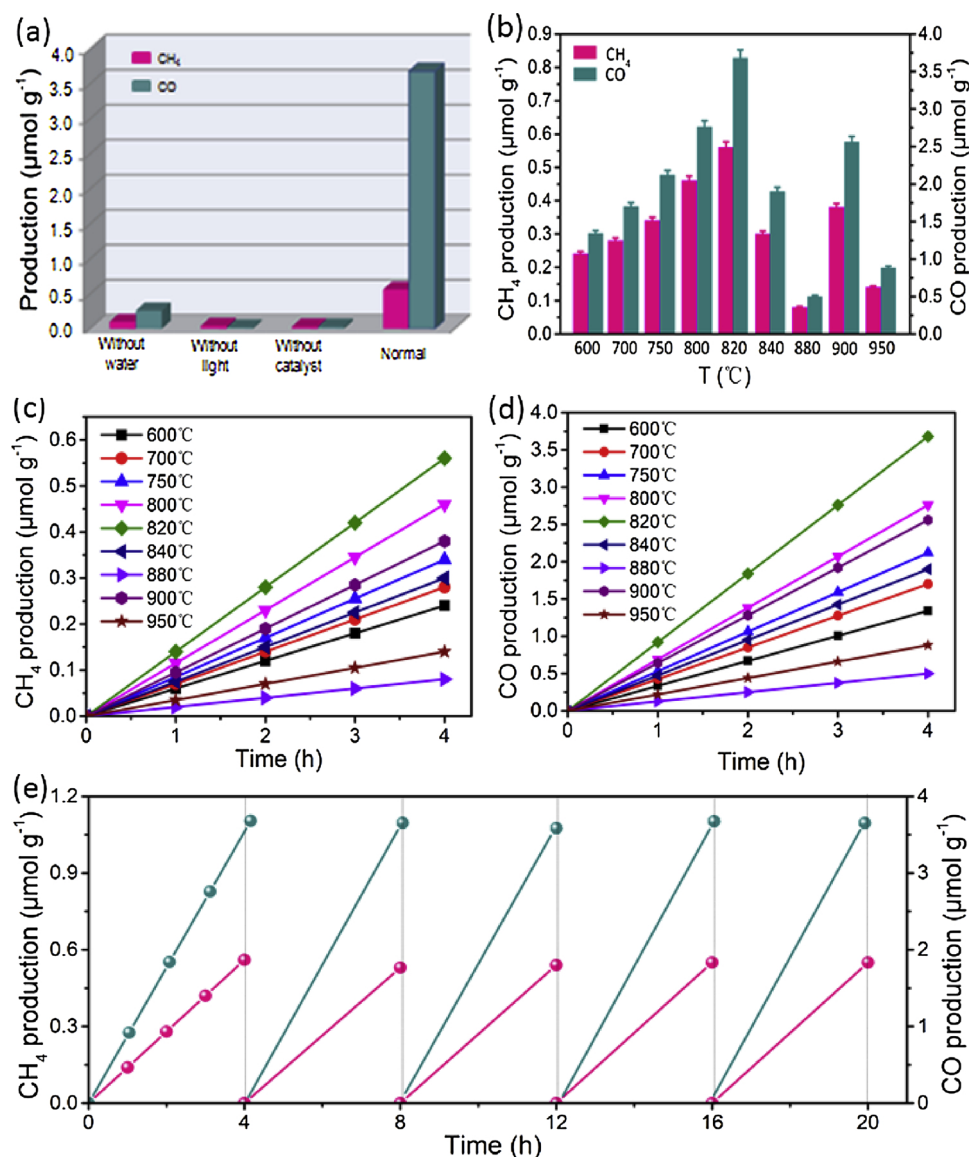


Fig. 7. Photocatalytic performance: (a) The CH₄ and CO yields under different conditions. (b) The CH₄ and CO yields after 4 h of UV light irradiation. The time courses of (c) photocatalytic CH₄ evolution and (d) CO production yield of various samples. (e) Cyclic use of photocatalyst for CO₂ reduction.

(Fig. 6g and h) reveal rod-like particles, consistent with XRD result. As presented in Fig. 6i, the lattice spacing of 0.324 nm can be assigned to the (110) crystal plane of Zn₂TiO₄ and the interplanar spacing of 0.489 nm corresponds the (111) plane of R-TiO₂. Additionally, the selected-area electron diffraction (SAED) patterns of the three spots (see the insets in Fig. 6b, e and h) suggest the single-crystalline nature of the as-synthesized Zn₂Ti₃O₈, Zn₂Ti₃O₈/ZnTiO₃ and Zn₂TiO₄/R-TiO₂ samples.

The zinc titanate-based heterostructures were employed as photocatalysts in CO₂ reduction under UV-light illumination (Fig. 7). Fig. 7a shows no products were detected without light irradiation or in the absence of the photocatalyst. This result suggests that light and titanate-based photocatalyst are both necessary in CO₂ reduction. In the absence of H₂O, it was observed that only a limited amount of CH₄ and CO were generated under the catalysis of Zn₂Ti₃O₈/ZnTiO₃ (obtained at 820 °C). When water was added, the amount of CO and CH₄ generated was significantly increased under UV-light irradiation. This result indicates that H₂O serves as hydrogen source and electron donor in the CO₂ photoreduction system [2,12]. The photocatalytic performance of commercial anatase TiO₂ (A-TiO₂) was also tested for comparison. The A-TiO₂ nanoparticles only showed a CO yield of ca. 0.93 μmol g⁻¹

(Figs. S2 and S3). Obviously, the zinc titanate-based heterostructured photocatalysts had a higher photocatalytic performance than A-TiO₂ in CO₂ reduction. The photoreduction measurements, photocatalytic performances of a series of zinc titanate-based heterostructured photocatalysts were evaluated. As displayed in Fig. 7b, pure Zn₂Ti₃O₈ merely showed a low CO of ca. 1.5 μmol g⁻¹ and a CH₄ yield of ca. 0.23 μmol g⁻¹ after 4 h of UV-light irradiation, whereas the heterostructured Zn₂Ti₃O₈/ZnTiO₃ prepared at 750–820 °C showed CO and CH₄ yields about two times of those pure Zn₂Ti₃O₈. Notably, the Zn₂Ti₃O₈/ZnTiO₃ obtained at 820 °C showed the highest photocatalytic performance, with CH₄ and CO yields up to 0.56 μmol g⁻¹ and 3.68 μmol g⁻¹, respectively. The CH₄ and CO production yields of Zn₂Ti₃O₈/ZnTiO₃ heterostructures obtained at 840 °C were lower than those of Zn₂Ti₃O₈/ZnTiO₃ heterostructures obtained at 820 °C. These results can testify the vital role of heterogeneous interfaces endowed by various phase compositions in improving the photocatalytic performance of photocatalyst. The results also demonstrate that the co-existence of optimized phase junctions between Zn₂Ti₃O₈ and ZnTiO₃ is of great importance to effectively enhance the photocatalytic performance of photocatalyst.

In addition, the photocatalytic performance of Zn₂TiO₄/R-TiO₂ heterostructure was evaluated. For comparison, the photocatalytic

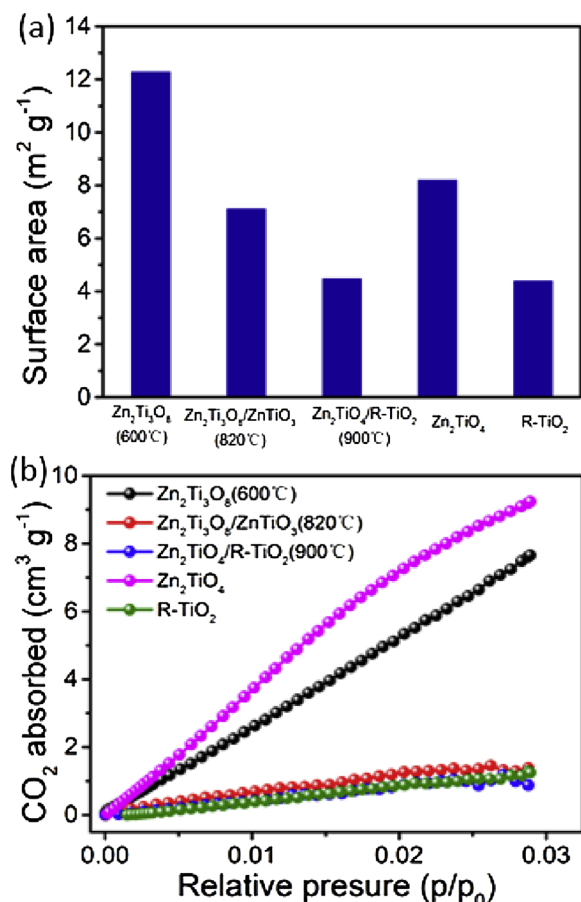


Fig. 8. The specific surface area (a) and CO₂ adsorption isotherms (b) of the as-prepared samples.

performance of R-TiO₂, Zn₂TiO₄, A-TiO₂ and R-TiO₂ + Zn₂TiO₄ (prepared by physical mixing) were also determined. The yields of CH₄ and CO under the catalysis of R-TiO₂, Zn₂TiO₄, A-TiO₂ and R-TiO₂ + Zn₂TiO₄ mixture are shown in Fig. S2. Pure R-TiO₂ shows no photocatalytic activity. The CO yield of A-TiO₂ was only 0.93 μmol g⁻¹. Furthermore, Zn₂TiO₄ and R-TiO₂/Zn₂TiO₄ composite obtained by physical mixing also showed poor photocatalytic activities in CO₂ photoreduction. However, the maximal CH₄ and CO yields were achieved under the catalysis of heterostructured Zn₂TiO₄/R-TiO₂ (calcined at 900 °C) and were 0.38 μmol g⁻¹ and 2.56 μmol g⁻¹, respectively (Fig. 7b). Fig. 7c and d show the CH₄ and CO yields changing with illumination time under the catalysis of various photocatalysts. It was found that the amount of products (CH₄ and CO) increased linearly with irradiation time. As compared with other catalysts, the obtained Zn₂Ti₃O₈/ZnTiO₃ (calcined at 820 °C) and Zn₂TiO₄/R-TiO₂ (calcined at 900 °C) exhibited higher photocatalytic performance in the conversion of CO₂ to CH₄ and CO in the presence of water.

As a photocatalyst, reusability and stability are important factors for practical applications. In order to investigate the durability of the photocatalyst Zn₂Ti₃O₈/ZnTiO₃ (calcined at 820 °C) was cyclically used for five times in CO₂ reduction. As shown in Fig. 7e, the photocatalytic activity of the photocatalyst did not decrease after five successive cycles, and the amount of products (CH₄ and CO) almost increased linearly with increasing irradiation time per cycle. These results confirm the high stability of zinc titanate-based heterostructures.

According to the SEM results (Fig. 5), the particle sizes of the prepared samples increase with increasing calcining temperature. The BET specific surface areas of the products decreased from 12.4 to 4.5 m² g⁻¹ as calcining temperature increases from 600 to 900 °C (Figs. S4 and 8 a). Combining the results in Figs. 5, 8a, S2, S3 and 7 b, we can find that the

photocatalytic activities of zinc titanate-based heterostructures are not directly related to their size or specific surface area. In addition, the amount of CO₂ adsorbed on the photocatalysts was measured by the BET method at 0 °C (Fig. 8b). The results show that the CO₂ adsorption capabilities of these photocatalysts are not consistent with the photocatalytic activity results reported above (Fig. 7b). This means that the enhanced photocatalytic activity of zinc titanate-based composites cannot be attributed to their CO₂ adsorption performance either. These results suggest that the surface-phase junctions may play a dominant role in promoting photogenerated charge separation and migration in the reaction of CO₂ with H₂O.

Diffuse reflectance spectroscopy (DRS) technique is one of the powerful tools for immediately observing the optical absorption properties of semiconductors from UV to visible light. In order to reveal the band gap energy E_g of zinc titanate-based samples, the UV-vis absorption spectra were obtained (Fig. 9a). According to the Kubelka-Munk equation: $\alpha h\nu = A(\alpha h\nu - E_g)^n$ [39], it can be deduced that the samples obtained at 600, 820 and 900 °C and R-TiO₂ have a band gap energy E_g of ca. 3.71, 3.62, 3.44 and 3.02 eV, respectively, corresponding to optical absorption edges of ca. 334, 342, 360 and 410 nm, respectively. Particularly, the DRS spectra of samples prepared at 820 and 900 °C both exhibit a shoulder peak at 350–400 nm, which may be due to that the samples were both composed of two different phases. The XPS valence band spectra of samples obtained are shown in Fig. 9b. It was estimated that the valence band potentials (E_{VB}) of samples obtained at 600 °C, 820 °C, and 900 °C and R-TiO₂ are ca. 2.68, 2.67, 2.39, and 2.65 eV, respectively. Therefore, the conduction band potential (E_{CB}) of above samples are about -1.03, -0.95, -1.05, and -0.37 eV, respectively, obtained by $E_g = E_{VB} - E_{CB}$. As shown in Fig. S4, the E_g and E_{VB} of Zn₂TiO₄ obtained at high temperature are 3.70 eV and 2.45 eV, and the E_{CB} of Zn₂TiO₄ is -1.25 eV. The E_{CB} and E_{VB} values are -0.46 eV and +3.19 eV for cubic ZnTiO₃, respectively [40]. It is worth noting that the redox potential of CO/CO₂ is -0.53 V vs. NHE at pH 7.0 [41], thus products prepared at 600, 820, and 900 °C and Zn₂TiO₄ can help transform CO₂ and H₂O to CO and CH₄, but ZnTiO₃ and R-TiO₂ cannot help transform CO₂ to CO. This was also demonstrated through the experimental results reported above (Figs. 7 and S5).

To characterize the interfacial electrochemical properties of electrodes, an electrochemical impedance spectrum (EIS) is generally used. Commonly, the smaller arc in an EIS Nyquist plot indicates a smaller charge-transfer resistance on the electrode surface [42,43]. Fig. 9c shows that the relationship between the arc sizes of the two electrodes is Zn₂Ti₃O₈/ZnTiO₃ < Zn₂Ti₃O₈. This indicates that the Zn₂Ti₃O₈/ZnTiO₃ heterostructure exhibits lower charge-transfer resistance than Zn₂Ti₃O₈ [42,43]. Similarly, as shown in Fig. 9d, the EIS spectra of Zn₂TiO₄/R-TiO₂ present a smaller arc than those of the bare R-TiO₂, suggesting that Zn₂TiO₄/R-TiO₂ heterostructure exhibit lower charge-transfer resistance [44,45]. It is important to note that the EIS results of these heterostructured samples are consistent with the photocatalytic activity results reported above (Fig. 7). Therefore, the zinc titanate-based heterostructures can effectively reduce the rapid recombination of electron-hole pairs within photocatalytic materials. As a result, more effective charge separation and transfer as well as higher photocatalytic performance are achieved.

In order to analyze in depth the working mechanism of the heterostructures prepared, the band gap structures of Zn₂Ti₃O₈/ZnTiO₃ and Zn₂TiO₄/R-TiO₂ were further studied. According to the above DRS and valence-band XPS spectra results, we propose here a possible route of CO₂ reduction, as shown in scheme 1.

The reduction of CO₂ usually proceeds in the presence of water. Commonly, the reduction potential of CO₂ (i.e., $E^0(\text{CO}_2/\text{CO}) = -0.53 \text{ V vs. NHE at pH} = 7.0$) and the oxidation potential of H₂O (i.e., $E^0(\text{O}_2/\text{H}_2\text{O}) = 0.82 \text{ V vs. NHE at pH} = 7.0$) should be considered to meet requirements of half-reaction of CO₂ reduction and half-reaction of water oxidation simultaneously [1,9]. On the basis of the detailed analysis of the band edge positions above (Fig. 9 and Scheme

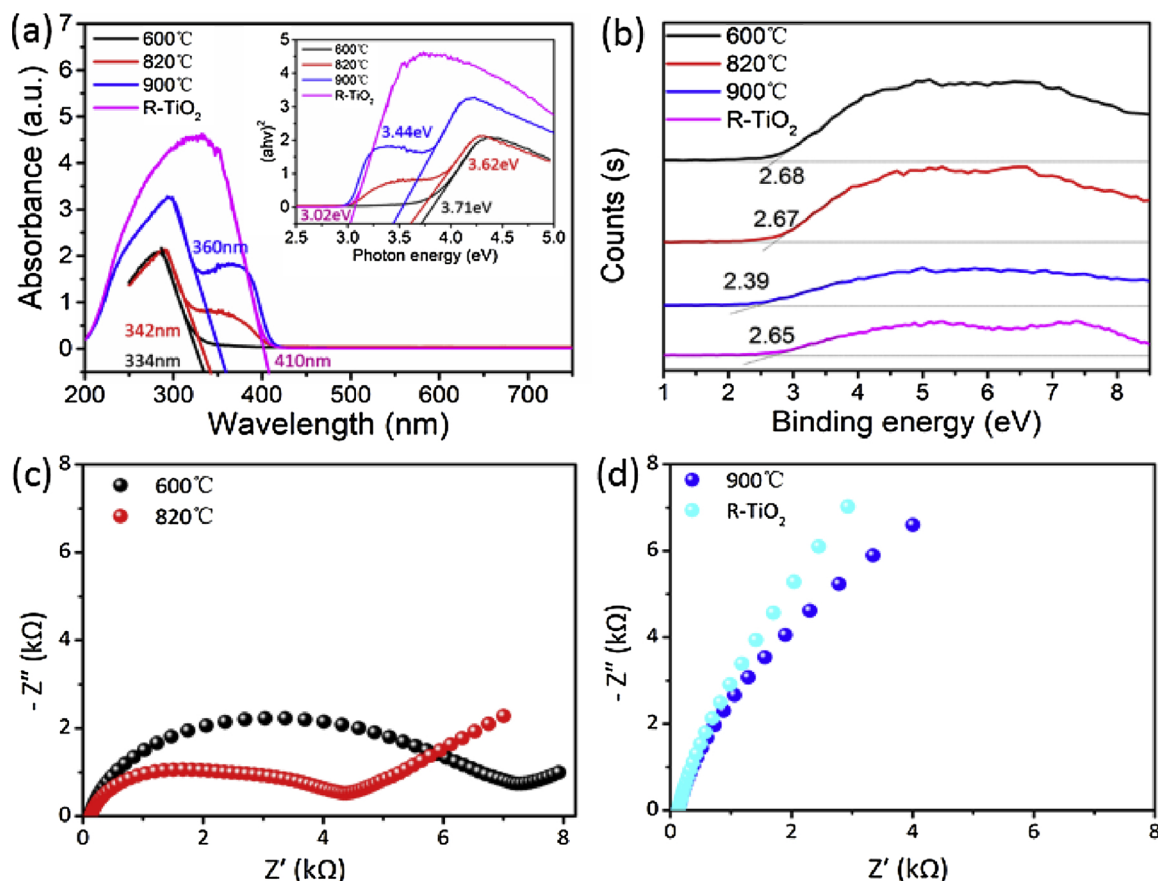
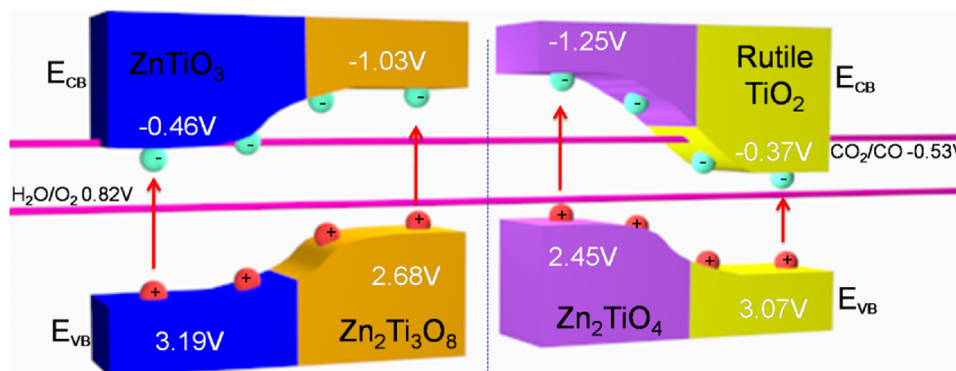


Fig. 9. (a) Diffuse absorption spectra of the samples obtained at 600 °C, 820 °C and 900 °C and R-TiO₂ (inset is the optical band gap energy E_g of corresponding samples). (b) Valence-band XPS spectra of corresponding samples. (c–d) Electrochemical impedance spectra of the samples obtained.



Scheme 1. Schematic illustration of charge separation and transfer pathway in Zn₂Ti₃O₈/ZnTiO₃ heterostructure (left) and Zn₂TiO₄/R-TiO₂ heterostructure (right).

1), ZnTiO₃ and R-TiO₂ cannot catalyze the photoreduction of CO₂ to CO because the E_{CB} potentials of ZnTiO₃ (-0.46 V vs. NHE) and R-TiO₂ (-0.37 V vs. NHE) are more positive than the standard redox potential $E^0(\text{CO}_2/\text{CO}) = -0.53$ V vs. NHE). However, Zn₂Ti₃O₈ ($E_{CB} = -1.03$ V vs. NHE) and Zn₂TiO₄ ($E_{CB} = -1.25$ V vs. NHE) are active phases and can catalyze CO₂ reduction. To take Zn₂Ti₃O₈/ZnTiO₃ as an example, the electrons and holes are generated at the Zn₂Ti₃O₈/ZnTiO₃ photocatalyst (eq. 1). Thermodynamically, in addition to the photogenerated electrons, the effect of the simultaneously photoinduced holes should be involved. The valence band of most semiconductors (e.g., Zn₂Ti₃O₈ ($E_{VB} = 2.68$ V vs. NHE)) is located well below the oxidation potential of water, whereas eq. 2 gives a value of 2.32 V ($E^0(\text{H}_2\text{O}/\cdot\text{OH}) = 2.32$ V vs. NHE) [46,47]. Therefore, in our case, at the surface the holes (h^+) can react with the adsorbed H₂O molecule to produce hydroxyl radicals ($\cdot\text{OH}$) and protons (H^+) (eq. 2) [2], and the electrons are involved in

reduction reaction with CO₂ to produce CH₄ and CO and oxidation reaction with H₂O to produce H^+ . The formation of CO and CH₄ requires $2\text{H}^+ / 2e^-$ and $8\text{H}^+ / 8e^-$ [48], respectively, according to eqs. (3) and (4). The proposed reactions involved in the CO₂ photoreduction to produce CH₄ and CO can be described by eqs. (1)–(4).



Upon the UV-light irradiation, both ZnTiO₃ and Zn₂Ti₃O₈ components in the Zn₂Ti₃O₈/ZnTiO₃ heterostructure are excited to generate charge carriers in their valence band (VB) and conduction band (CB),

respectively. Those components alone present poor photocatalytic performance owing to the direct recombination of most photo-induced electron-hole pairs. After the $\text{Zn}_2\text{Ti}_3\text{O}_8/\text{ZnTiO}_3$ heterojunction was constructed, the photoelectrons of $\text{Zn}_2\text{Ti}_3\text{O}_8$ in the CB could readily migrate to the CB position of ZnTiO_3 through the interface electronic field, resulting in effective separation of charges through heterojunction. Meanwhile, the photoelectrons and holes are gathered on CB position of ZnTiO_3 and VB position of $\text{Zn}_2\text{Ti}_3\text{O}_8$, respectively. This means that the synergistic effect of the $\text{Zn}_2\text{Ti}_3\text{O}_8/\text{ZnTiO}_3$ heterostructure may promote efficient separation and transfer of photoinduced charges and therefore restrain the recombination of photogenerated electron-hole pairs, resulting in an enhanced photocatalytic activity in CO_2 -reduction. In view of the above results, the approximate band-edge positions of the $\text{Zn}_2\text{Ti}_3\text{O}_8$, ZnTiO_3 , Zn_2TiO_4 and R-TiO_2 are displayed in [scheme 1](#), demonstrating that the $\text{Zn}_2\text{Ti}_3\text{O}_8/\text{ZnTiO}_3$ heterostructure and $\text{Zn}_2\text{TiO}_4/\text{R-TiO}_2$ heterostructure facilitate directed charge carrier transport and suppress charge recombination by Ti-O bonding at the atomic level, thus promoting CO_2 reduction [49].

To gain more atomic insight into the electron-hole transport mechanism, the electronic structures of $\text{Zn}_2\text{Ti}_3\text{O}_8/\text{ZnTiO}_3$ and $\text{Zn}_2\text{TiO}_4/\text{R-TiO}_2$ were studied by density functional theory (DFT) calculations (Figs. S6 and S7). The calculated densities of states (DOS) of individual $\text{Zn}_2\text{Ti}_3\text{O}_8$, ZnTiO_3 , Zn_2TiO_4 , R-TiO_2 , $\text{Zn}_2\text{Ti}_3\text{O}_8/\text{ZnTiO}_3$ and $\text{Zn}_2\text{TiO}_4/\text{R-TiO}_2$ reveal typical semiconductor characteristics with band-gap of less than 4 eV (Table S1). As for the $\text{Zn}_2\text{Ti}_3\text{O}_8/\text{ZnTiO}_3$ heterostructure, the band gap is about 3.50 eV. As shown in the Fig. S7e, the contribution of Zn atoms is smaller than that of Ti atoms. In comparison with pure $\text{Zn}_2\text{Ti}_3\text{O}_8$ and ZnTiO_3 , $\text{Zn}_2\text{Ti}_3\text{O}_8/\text{ZnTiO}_3$ shows reduced band gap, implying that the heterostructure can increase the wavelength of absorbed light, thereby achieving higher photoconversion efficiency. As for the DOS of $\text{R-TiO}_2/\text{Zn}_2\text{TiO}_4$ heterostructure, the band gap is about 3.0 eV, which is close to the experiment value, and the conduction band and the valence band are mainly composed by the Ti and O atoms. Hence, based on the experimental analysis and theoretical calculations, we can conclude that the heterostructure is much better for the separation of electrons and holes than the others.

4. Conclusions

In sum, we reported the synthesis of $\text{Zn}_2\text{Ti}_3\text{O}_8/\text{ZnTiO}_3$ and $\text{Zn}_2\text{TiO}_4/\text{R-TiO}_2$ heterostructures via a facile hydrothermal reaction of butyl titanate with zinc acetate, followed by high-temperature calcinations under air flow. Subsequent detailed investigations show that the heterostructured nanohybrids possess explicit heterointerfaces and tunable band edges. When used as photocatalysts towards the reduction of CO_2 with H_2O under UV-light irradiation, the nanocrystalline $\text{Zn}_2\text{Ti}_3\text{O}_8/\text{ZnTiO}_3$ and $\text{Zn}_2\text{TiO}_4/\text{R-TiO}_2$ heterostructures show high photocatalytic performance, with CH_4 and CO yields of $0.56 \mu\text{mol g}^{-1}$ and $3.68 \mu\text{mol g}^{-1}$, as well as $0.38 \mu\text{mol g}^{-1}$ and $2.56 \mu\text{mol g}^{-1}$, respectively, after 4 h of UV-light irradiation. The band gap structures and the working mechanisms of $\text{Zn}_2\text{Ti}_3\text{O}_8/\text{ZnTiO}_3$ and $\text{Zn}_2\text{TiO}_4/\text{R-TiO}_2$ heterostructures were proposed. The present work indicates that the enhanced photoactivity may be resulted from the efficient separation of photoinduced electron-hole pairs derived from the constructed zinc titanate heterostructures. This work would provide a significant strategy to effectively convert CO_2 into fuels by using rationally designed heterostructures.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2019.117800>.

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